Theoretische Modellierung und Simulation

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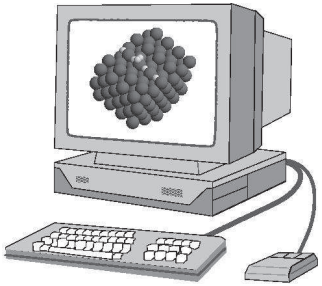


1. Einführung
2. Lehrplan
3. Vorlesung

Computational Quantum chemistry

Virtual chemistry lab

Inst. f. Theoretische Chemie, O25

Computational Chemistry

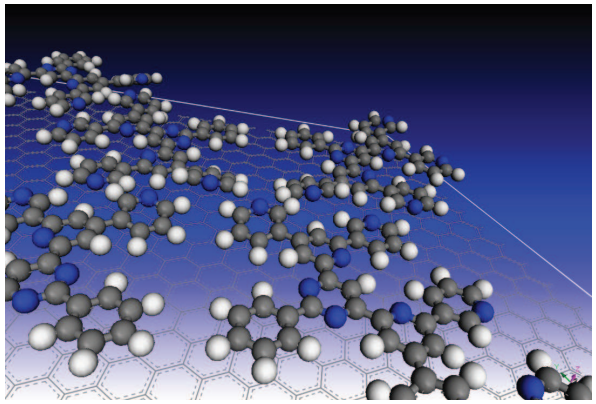
- Evaluation of the electronic, geometric and chemical porperties of molecules, surfaces and solids with modern methods of electronic structure theory
- Quantum chemical program packages (Gaussian, NWChem, . . .) and Plane-Wave-Methods (VASP, Abinit, . . .)
- Empirical programs, e.g. force fields and code development
- Analysis and visualisation of the results

Contents

1. Introduction
2. Molecular Modeling
3. Statistical Mechanics and Monte Carlo methods
4. Molecular dynamics
5. Quantum Mechanics
6. Multiscale Modeling

Adsorption of organic molecules

Study of the electronic, chemical, catalytic and optic properties of organic molecules on anorganic substrates

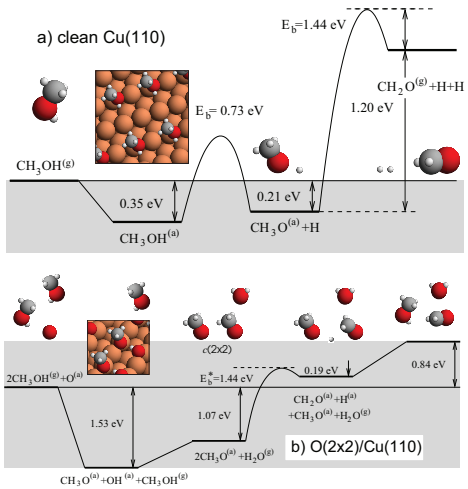


Structure of oligopyridine on graphite

Close collaboration with experimental groups

Surface reactions: Methanol oxidation on O(2×2)/Cu(110)

S.Sakong and A. Groß, J. Catal. **231**, 420 (2005).



Energy scheme of the partial oxidation of CH_3OH on clean and (2×2) oxygen-precovered Cu(110)

Exhaust catalyst

Structure of the exhaust catalyst

Elementary steps in the CO oxidation

Without movies

Schematic animation of the CO oxidation
(C.Stampfl, FHI Berlin)

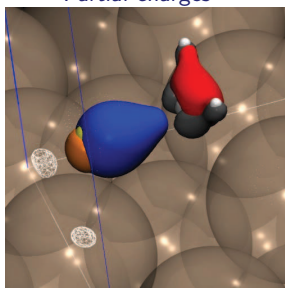
H.-J. Freund, Surf. Sci. **500**, 271 (2002)

Methanol oxidation on Cu: Analysis of the electronic structure

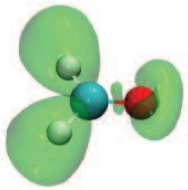
S.Sakong and A. Groß, J. Catal. **231**, 420 (2005).

CH_2O/Cu(110): Chemical interaction analyzed using electronic orbitals and charge densities

Partial charges



Electron localisation



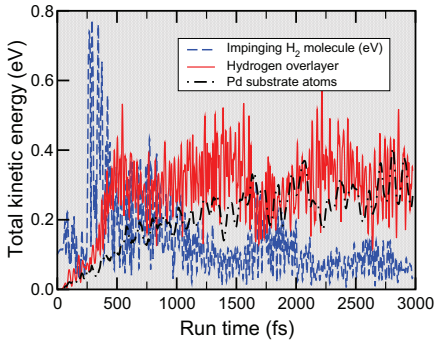
Detection of the electronic factors that determine the reactivity

Adsorption of H_2/(3×3)7H/Pd(100)

Dissociation

Without movies

Energy redistribution



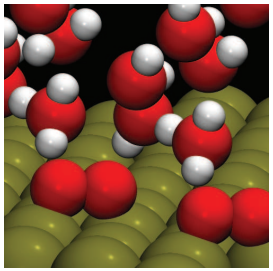
Large energy transfer to the hydrogen layer upon the dissociative adsorption of H_2

Weak H-Pd coupling: hydrogen layer still not in thermal equilibrium after 3 ps

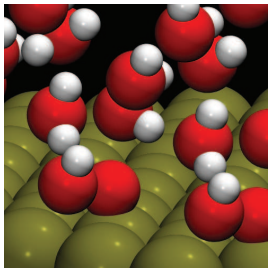
Elektrochemistry and electro catalysis

Interaction O_2 with a Zundel ion on Pt(111) in an aqueous environment

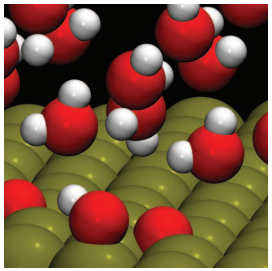
Initial configuration



Adsorbed OOH



Adsorbed O + OH



Presence of water leads to activation barriers for the oxygen reduction on Pt(111)

Study of systems that are relevant for the electrochemical energy conversion and storage

Quantum Mechanics: Hamiltonian

Chemistry:
Only electrostatic interaction taken into account ⇒ Hamiltonian:

$$H = T_{\mathrm{nucl}} + T_{\mathrm{el}} + V_{\mathrm{nucl-nucl}} + V_{\mathrm{nucl-el}} + V_{\mathrm{el-el}} \tag{1}$$

$$T_{\mathrm{nucl}} = \sum_{\mathrm{I}=1}^{L} \frac{\vec{P}_{\mathrm{I}}^2}{2M_{\mathrm{I}}} = \sum_{\mathrm{I}=1}^{L} \frac{-\hbar^2}{2M_{\mathrm{I}}} \vec{\nabla}_{\mathrm{I}}^2, \tag{2}$$

$$T_{\mathrm{el}} = \sum_{\mathrm{i}=1}^{N} \frac{\vec{p}_{\mathrm{i}}^2}{2m} = \sum_{\mathrm{i}=1}^{N} \frac{-\hbar^2}{2m_{\mathrm{i}}} \vec{\nabla}_{\mathrm{i}}^2, \tag{3}$$

$$V_{\mathrm{nucl-nucl}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\mathrm{I}\neq\mathrm{J}} \frac{Z_{\mathrm{I}}\, Z_{\mathrm{J}}\, e^2}{|\vec{R}_{\mathrm{I}} - \vec{R}_{\mathrm{J}}|}, \tag{4}$$

$$V_{\mathrm{nucl-el}} = -\frac{1}{4\pi\epsilon_0} \sum_{\mathrm{i,I}} \frac{Z_{\mathrm{I}}\, e^2}{|\vec{r}_{\mathrm{i}} - \vec{R}_{\mathrm{I}}|}, \tag{5}$$

$$V_{\mathrm{el-el}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\mathrm{i}\neq\mathrm{j}} \frac{e^2}{|\vec{r}_{\mathrm{i}} - \vec{r}_{\mathrm{j}}|}. \tag{6}$$

Ab initio molecular dynamics simulations of H_2 dissociation on water-covered Pt(111)

Trajectory

Without movies

Discussion

H_2 dissociation through thermalized disordered water layer

After dissociation, H atoms can move almost freely beneath the water layer

H atoms end up at top sites

Disordered water layer rearranges upon H adsorption

Schrödinger Equation

Nonrelativistic Schrödinger Equations:

$$H\ \Psi(\vec{R}, \vec{r}) = E\ \Psi(\vec{R}, \vec{r}). \tag{7}$$

$$i\hbar \frac{\partial \Psi(\vec{R}, \vec{r}, t)}{\partial t} = H\ \Psi(\vec{R}, \vec{r}). \tag{8}$$

Solution: Eigen and initial value problem, respectively, of a high-dimensional partial differential equation taking into account the appropriate quantum statistics (→ Pauli principle)

In principle we are ready here, however

Solution of Schrödinger equation in closed form not possible

⇒ Hierarchy of approximate and numerical methods

Theoretical Chemistry

P.A.M Dirac (1930):

"The underlying physical laws necessary for the mathematical theory of a large part of physics *and the whole of chemistry* are thus completely know, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

Born-Oppenheimer approximation II

Schrödinger equation for the electrons

$$H_{\rm el}(\{\vec{R}\})\ \Psi(\vec{r},\{\vec{R}\}) \ = \ E_{\rm el}(\{\vec{R}\})\ \Psi(\vec{r},\{\vec{R}\}). \tag{11}$$

$E_{\rm el}(\{\vec{R}\})$ Born-Oppenheimer energy surface: potential for the nuclear motion:

$$\{T_{\rm nucl} + \ E_{\rm el}(\vec{R})\}\ \chi(\vec{R}) \ = \ E_{nucl}\ \chi(\vec{R}). \tag{12}$$

If quantum effects negligible: classical equation of motion

$$M_{\rm I}\ \frac{\partial^2}{\partial t^2}\vec{R}_I \ = \ -\frac{\partial}{\partial \vec{R}_I} E_{\rm el}(\{\vec{R}\}) \quad . \tag{13}$$

Born-Oppenheimer approximation

Atoms 10^4 to 10^5 heavier than electrons
(except for hydrogen and helium)

$\Rightarrow$electrons are 10^2 to 10^3 times faster than the nuclei

Born-Oppenheimer of adiabatic approximation:
electrons follow motion of the nuclei instantaneously

Practical implementation:
Define electronic Hamiltonian $H_{\rm el}$ for fixed nuclear coordinates $\{\vec{R}\}$

$$H_{\rm el}(\{\vec{R}\}) \ = \ T_{\rm el} \ + \ V_{\rm nucl-nucl} \ + \ V_{\rm nucl-el} \ + \ V_{\rm el-el}. \tag{9}$$

Nuclear coordinates $\{\vec{R}\}$ do not act as variables but as parameters
The Schrödinger equation for the electrons

$$H_{\rm el}(\{\vec{R}\})\ \Psi(\vec{r},\{\vec{R}\}) \ = \ E_{\rm el}(\{\vec{R}\})\ \Psi(\vec{r},\{\vec{R}\}). \tag{10}$$

Born-Oppenheimer approximation (BOA) III

In the BOA electronic transitions neglected

Exact derivation: Expansion of Schrödinger equation in the small parameter m/M

BOA very successful, but still its validity hardly directly obvious

Physical arguments

Systems with a band gap: electronic transitions improbable

Metals: electronic system strongly coupled
$\Rightarrow$ short lifetimes and fast quenchening of electronic excitations

Interaction between molecules

Consider ions A and B with charge Q_A and Q_B, respectively

$$\vec{R}_{AB} = \vec{R}_B - \vec{R}_A, R_{AB} = |\vec{R}_{AB}|$$

Force of Q_A acting on Q_B

$$\vec{F}_{AB} = \frac{1}{4\pi\epsilon_0}\frac{Q_A Q_B}{R_{AB}^3}\vec{R}_{AB} \quad (14)$$

Force of Q_B acting on Q_A

$$\vec{F}_{BA} = \frac{1}{4\pi\epsilon_0}\frac{Q_A Q_B}{R_{AB}^3}\vec{R}_{BA} \quad (15)$$

$$F_{BA} = \frac{1}{4\pi\epsilon_0}\frac{Q_A Q_B}{R_{AB}^2} \quad (16)$$

Pairwise additive forces
Force of Q_A and Q_C acting on Q_B

$$\vec{F}_B = \frac{Q_B}{4\pi\epsilon_0}\left(Q_a\frac{\vec{R}_{AB}}{R_{AB}^3} + Q_C\frac{\vec{R}_{CB}}{R_{CB}^3}\right) \quad (17)$$

Charge distribution

$$Q_A = \int \rho(\vec{r})d^3r \quad (18)$$

Force of Q_A acting on Q_B

$$\vec{F}_{AB} = \frac{Q_B}{4\pi\epsilon_0}\int \rho(\vec{r})\frac{(\vec{R}_B - \vec{r})}{|\vec{R}_B - \vec{r}|^3}d^3r \quad (19)$$

Many body interaction

Consider system of N atoms; If forces are additive

$$U_{\text{tot}} = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} U_{ij} = \frac{1}{2}\sum_{i\neq j}^{n,n} U_{ij} \quad (23)$$

General case

$$U_{\text{tot}} = U(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_n) \quad (24)$$

Formal expansion

$$U_{\text{tot}} = \sum_{\text{pairs}} U^{(2)}(\vec{R}_i, \vec{R}_j) + \sum_{\text{triples}} U^{(3)}(\vec{R}_i, \vec{R}_j, \vec{R}_k) + \ldots + U^{(n)}(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_n) \quad (25)$$

Nature of the interaction

$$U = U_{\text{es}} + U_{\text{disp}} + U_{\text{rep}} \quad (26)$$

Potential energy

$$U_{AB} = \frac{1}{4\pi\epsilon_0}\frac{Q_A Q_B}{R_{AB}} \quad (20)$$

Corresponds to the energy it costs to bring the two charges from infinity to the distance R_{AB}

Relation between force and potential energy; Energy in one dimension:

$$E = \frac{m}{2}v^2 + U(x) \quad (21)$$

Energy conservation, i.e. $dE/dt = 0$:

$$F = -\frac{dU}{dx}, \text{ in three dimensions}: \vec{F} = -\nabla U = -\left(\frac{\partial U}{\partial x}, \frac{\partial U}{\partial y}, \frac{\partial U}{\partial z}\right) \quad (22)$$

Force is directed along the steepest decent of U

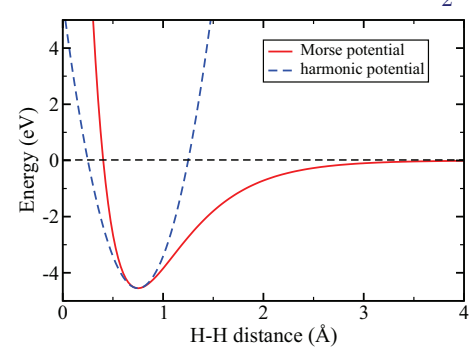
Vibrational potentials

Harmonic potential

$$U_{\text{vib}} = \frac{1}{2}k(R - R_e)^2 \text{ , } E_{\text{vib}} = \hbar\omega(v + \frac{1}{2}) \quad (27)$$

Morse potential, $\beta = \frac{\omega}{2}\sqrt{2\mu/D_e}$

$$U_{\text{vib}} = D_e\left[1 - \exp(-\beta(R - R_e))\right]^2 \text{ , } E_{\text{vib}} = \hbar\omega(v + \frac{1}{2}) - \chi_e\hbar\omega(v + \frac{1}{2})^2 \quad (28)$$



Molecular mechanics and force fields

Molecular Mechanics:

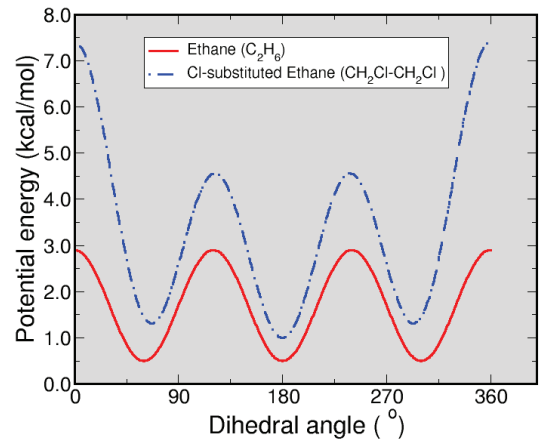
Application of classical mechanics to determinations of molecular equilibrium properties

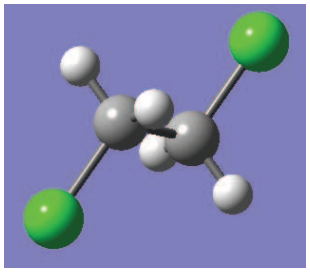
Force field: Parametrized interaction potential

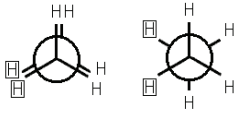
$$
\begin{aligned}
U &= \sum_{\text{stretch}} U_{\text{AB}} + \sum_{\text{bend}} U_{ABC} + \sum_{\text{dihedral}} U_{ABCD} + \sum_{\text{inversion}} U_{ABCD} + \\
&\quad + \sum_{\text{nonbonded}} U_{AB} + \sum_{\text{Coulomb}} U_{AB} + \qquad (29) \\
&= \sum_{\text{bonds}} \frac{1}{2} k_{AB}(R_{AB} - R_{e,AB})^2 + \sum_{\text{bends}} \frac{1}{2} k_{ABC}(\Theta_{ABC} - \Theta_{e,ABC})^2 \\
&\quad + \sum_{\text{dihedrals}} \frac{U_0}{2}(1 - \cos(n(\chi - \chi_0))) + \sum_{\text{inversions}} \frac{k}{2\sin^2\psi_e}(\cos\psi - \cos\psi_e)^2 \\
&\quad + \sum_{\text{nonbonded}} \left(\frac{C^{12}_{AB}}{R^{12}_{AB}} - \frac{C^{6}_{AB}}{R^{6}_{AB}}\right) + \sum_{\text{charges}} \frac{1}{4\pi\epsilon_0}\frac{Q_A Q_B}{R_{AB}} \qquad (30)
\end{aligned}
$$

Potential curves

Torsional potential Ethane and chlorine-substituted ethane



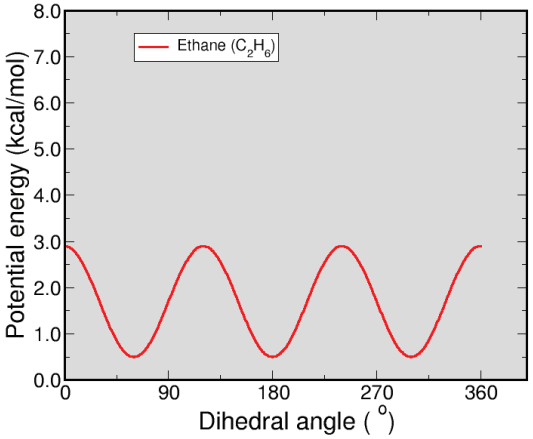


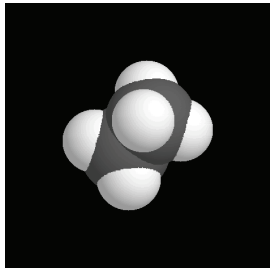


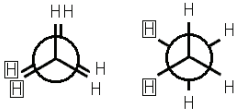
Multiple minima

Potential curves

Torsional potential Ethane



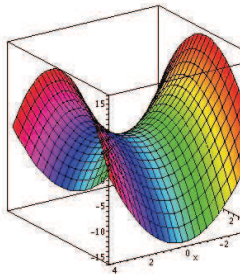


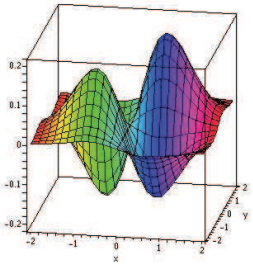


Multiple minima

Potential energy surfaces (PES)

Saddle point Two minima Multiple minima





Saddle points correspond to transition states in chemical reaction, minima to (meta)-stable intermediates

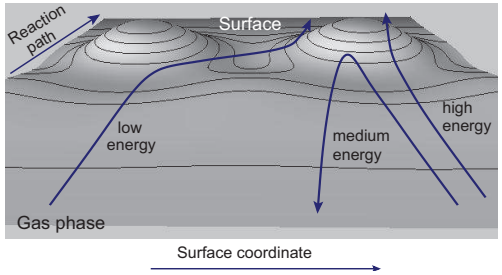
Reaction barriers are calculated as the difference between the the lowest saddle point towards the product state and the energy minimum corresponding to the reactant state

$$E_{\text{barr}} = E_{\text{TS}} - E_{\text{ini}} \qquad (31)$$

Sticking probability of H_2 on Pd(100)

Comparison theory-experiment

Steering effect



Exp.: K.D. Rendulic *et al.*, Surf. Sci. **208**, 404 (1989),
Theory: A. Groß *et al.*, PRL **75**, 2718 (1995).

All *six* hydrogen degrees of freedom treated quantum dynamically

Initial decrease in $S(E_\mathrm{i})$ caused by the suppression of the steering effect

Oscillations quantum effect: opening of new scattering channels with increasing energy

Potential energy surfaces

Complex PES, for example describing a polymer or protein

Finding minima and saddle points of potential energy surfaces is crucial for the determination of energy minimum structures and reaction barriers

Tight-binding molecular dynamics simulations: O_2/Pt(111)

A. Groß, A. Eichler, J. Hafner, M.J. Mehl, and D.A. Papaconstantopoulos, Surf. Sci. Lett. **539**, L542-L548 (2003).

Sticking probability

Dissociation?

Comparison of calculated and measured sticking probability as a function of the kinetic energy

Over the whole energy range sticking probability is determined by the trapping into the molecular chemisorption states

Projection of a trajectory of a O_2 molecule onto the Zd plane, initial kinetic energy $E_\mathrm{kin} = 0.6$ eV

O_2 molecules do not directly dissociate on Pt(111) because of steric hindrance
$\rightarrow$ dissociation of O_2/Pt(111) is a two-step process involving thermalisation

Characterization of potential energy surfaces

$p = 3n - 6$ degrees of freedom, Coordinates $\mathbf{q}$ and gradient $\mathbf{g}$:

$$\mathbf{q} = \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_p \end{pmatrix}, \qquad \mathbf{g} = \begin{pmatrix} \frac{\partial U}{\partial q_1} \\ \frac{\partial U}{\partial q_2} \\ \vdots \\ \frac{\partial U}{\partial q_p} \end{pmatrix}. \tag{32}$$

At stationary points, the gradient is zero

Characterization of stationary points: Calculate Hesse matrix at that points:

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 U}{\partial q_1^2} & \cdots & \frac{\partial^2 U}{\partial q_1 \partial q_p} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial q_p \partial q_1} & \cdots & \frac{\partial^2 U}{\partial q_p^2} \end{pmatrix}. \tag{33}$$

Eigenvalues all positive $\Rightarrow$ Minimum, Eigenvalues all negative $\Rightarrow$ Maximum, $\Rightarrow$ Maximum otherwise $\Rightarrow$ Saddle point

Transition state (barrier): Hesse matrix has exactly one negative eigenvalue

Finding minima

Finding minima = Optimization problem

Grid methods: multivariate and univariate grid search

Derivative methods

First-order methods

Steepest descent: Search minina along the negative of the gradient Problem: many perpendicular steps

Solution: Conjugate gradient method:

In k-th iteration, move in direction given by

$$\mathbf{v}^{(k)} = -\mathbf{g}^{(k)} + \gamma^{(k)}\mathbf{v}^{(k-1)}, \quad \gamma^{(k)} = \frac{\left(\mathbf{g}^{(k)}\right)^{\mathrm{T}}\mathbf{g}^{(k)}}{\left(\left(\mathbf{g}^{(k-1)}\right)^{\mathrm{T}}\mathbf{g}^{(k-1)}\right)} \tag{34}$$

Conjugate directions: perpendicular in isotropic configuration space

Green: steepest descent

Green: conjugate gradient

Second-order methods

Computationally more expansive since second derivative is required

Further methods: Simulated annealing, Monte Carlo methods, generic algorithms, . . .

Molecular Mechanics (MM)

Molecular Mechanics (MM) useful for the determination of possible equilibrium properties of molecules

Many software packages available

Commercial products often offer convenient graphical user interfaces (GUI)

GaussView (GAUSSIAN) Materials Visualizer (Materials Studio)

Besides MM programmes, often quantum chemistry codes included in the packages

Finding transition states

There is no analytical method that guarentees to find the nearest transition states ⇒ approximate schemes

Nudged elastic band method

http://theory.cm.utexas.edu/henkelman/research/saddle/

The Nudged Elastic Band (NEB) method is used to find minimum energy path (NEB) when both the initial and final states are known.

G. Henkelman and H. Jonsson, J. Chem. Phys. **113**, 9978 (2000).

The code works by linearly interpolating a set of images between the initial and final states (as a "guess" at the MEP), and then minimizes the energy of this string of images connected by springs.

Each "image" corresponds to a specific geometry of the atoms on their way from the initial to the final state.

Once the energy of this string of images has been minimized, the true MEP is revealed.

Further methods: Dimer method

Statistical Mechanics

Statistical mechanics provides a relation between microscopic (atomistic) and macroscopic description of matter using mean values and deviations

Statistical description ⇒ Mean values of significant importance

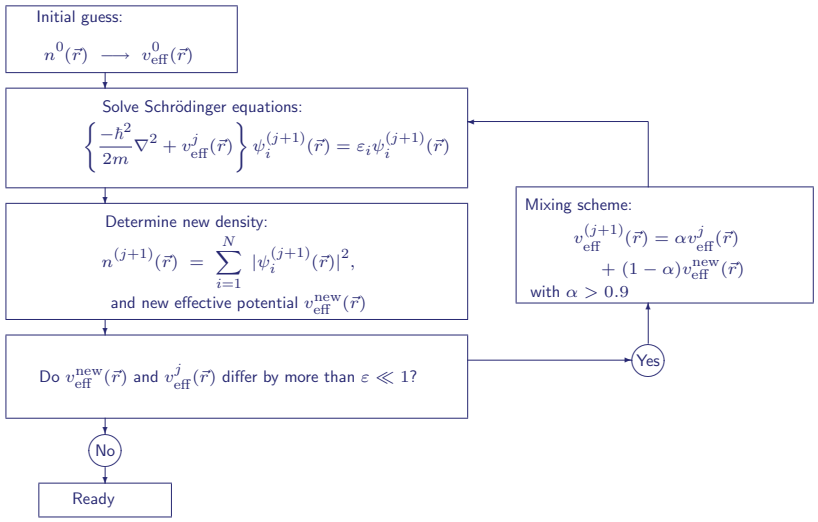
Mean value $< x >$:

$$< x > = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{35}$$

Root mean square deviations (fluctuations):

$$\sigma_n = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - < x >)^2} \tag{36}$$

Central entity in statistical mechanics: **ensemble**

Self-consistent field (SCF) solution

Effective one-particle Hartree-Fock Hamiltonians contain solution: $\Rightarrow$ SCF iteration scheme